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*Department of Chemistry*
*Washington, D.C. 20064*

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Progress Report

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# Studies of Elementary Reactions of Chemical Importance in the Atmospheres of Planets

Fred L. Nesbitt, Principal Investigator

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**Progress Report**
**Fred L. Nesbitt**
**1 May 2002 – 30 April 2003**

**F + $Cl_2$ Kinetics**
Absolute rate constant for the reaction $F(^2P)$ with $Cl_2$ has been measured using the discharge flow kinetics technique coupled to mass spectrometric detection at T = 180 – 360 K and 1 Torr He nominal pressure. Experiments were performed at NASA Goddard Space Flight Center (GSFC) in Greenbelt, Maryland USA and Laboratoire de Combustion et Systemes Reactifs-CNRS in Orleans, France. Results of k = $(5.7\pm0.8)\times10^{-11}$ and $(6.2\pm0.8)\times10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ independent of temperature were obtained by each laboratory, respectively. When the results from both laboratories were combined into one dataset, an average temperature independent value of $k_1 = (6.0\pm 1.1)\times10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ was obtained. A very slight positive temperature dependence with $k_1(T) = (6.5\pm1.5)\times10^{-11} \exp\{-(20\pm60)/T\}$ $cm^3 molecule^{-1} s^{-1}$ may also be derived from the combined data in the range T = 180 – 360 K.

From the GSFC laboratory the average temperature independent rate constant is $k_1 = (5.7 \pm 0.8)\times10^{-11}$ $cm^3$ $molecule^{-1}s^{-1}$. An Arrhenius plot of this data for the temperature range T = 180 – 298 K shows a relatively flat temperature dependence. For the results from the CNRS laboratory the least square analysis of the data provides the Arrhenius expression : $k_1 = (4.8 \pm0.5)\times10^{-11} \exp\{(70 \pm 60)/T\}$ $cm^3 molecule^{-1}s^{-1}$ for T = (230-360) K, where the quoted uncertainties represent $2\sigma$ for the activation energy and $1\sigma$ for the preexponential factor. Thus, this shows no more than a small negative temperature dependence of the rate constant of the F + $Cl_2$ reaction. In fact, considering the experimental uncertainty, the temperature independent value of $k_1 = (6.2 \pm 0.8)\times10^{-11}$

$cm^3 molecule^{-1} s^{-1}$ at T = (230-360) K can be also recommended from the CNRS set of results.

When the two sets of laboratory results from CNRS and GSFC are combined and treated as one set of results, the average temperature independent value derived for $k_1$ is $(6.0 \pm 1.1) \times 10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ for the temperature range of 180 - 360 K. The least square analysis of the combined results provides the following Arrhenius expression with a very weak positive temperature dependence:

$$k_1 = (6.5 \pm 1.5) \times 10^{-11} \exp\{-(20 \pm 60)/T\}\ cm^3 molecule^{-1} s^{-1} \qquad T = (180\text{-}360)\ K$$

The results for the rate constant for this reaction from this study differ significantly from those previously published. The only other temperature study is that of Warnatz et al in a discharge flow - mass spectrometer system that covered a temperature range from T = 232 to 350 K. This earlier study measured a much steeper temperature dependence for $k_1$ than was found in this present work. Their derived Arrhenius expression is:

$$k_1 = 9.1 \times 10^{-10} \exp(-700/T\}\ cm^3 molecule^{-1} s^{-1} \text{ at } T = (232\text{-}373)\ K$$

where the activation energy is more than a factor of ten greater than that derived in this work. A study by Appelman and Clyne measured a value of $1.6 \times 10^{-10}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ at T = 298 K in a discharge flow - mass spectrometer system; this value of $k_1$ is about a factor of two greater than that measured in this present study.

It is generally accepted that there is no secondary chemistry in the $F + Cl_2$ reaction system. In addition, the previous studies as well as the present one all employed the same experimental technique of discharge flow – mass spectrometry. Therefore, there is no obvious explanation for the discrepancy in the values of $k_1$ between those from the present study and those from the earlier studies.

This work has been submitted and accepted for publication in the Journal of Physical Chemistry. Other studies in progress are the reaction of $CH_3 + C_2H_5$ and the reaction of H + $C_2H_3$.

**Progress report**
**Robert N. Nelson, Ph.D.**
**1 May 2002 – 30 April 2003**

**Vapor pressure system**

The main effort on the vapor pressure system involved the design and construction of an insulated enclosure ("Bakeout Box") to improve the uniformity of heating during the bakeout process. This insulated enclosure ensures that the entire manifold is exposed to uniform temperature during the bakeout process so that there is no accumulation of outgassed material in cold spots. With the new system, we were able to achieve lower base pressures than in the past ($<1x10^{-7}$ torr vs. $5x10^{-7}$ torr) and were able to determine that there appear to be two possible small leaks. One is most likely a cracked bellows connecting the manifold to the pumping system and is only of importance during pumpout operations since the bellows section is valved out during measurement. The other is much smaller and is probably a slight gasket defect on the spinning rotor gauge. This one is very small ($<1x10^{-8}$ torr/sec) and can be calibrated out during measurements.

**Sunphotometer System**

This period saw the completion of the two-channel sunphotometer, its calibration, and two field deployments. The two-channel system offers continuous and overlapping coverage from 400-1200 nm in the visible and from 1100 – 4400 nm (1.1 – 4.4 μm) in the infrared. The calibration was carried out using both continuous blackbody light sources and lasers. The blackbodies included a calibrated 1500 K blackbody source and a quartz-tungsten-halogen lamp which was calibrated against the 1500 K blackbody. In the summer of 2002 the instrument was installed at the GSFC Optical Site for measurements and testing. After some modifications and repairs to the equatorial mount, Robert Nelson, John Allen (GSFC), and Cheyenne Harris (GSFC) took the instrument to Appalachian State University in Boone, NC in April of 2003. There we obtained not only multiple measurements on atmospheric transmission but also measurements of visible light scattering and polarization. We are currently updating the instrument with a new visible detector to replace one that failed in July 2003.

**Progress Report**
**Benjamin P. Michael**
**1 May 2002 – 30 April 2003**

Vibrational-to-translation (V-T) transfer rates for light hydrocarbons at low temperatures are important parameters in thermal-structure models of the upper atmospheres of the outer planets and their satellites. However, the required data are either simply not available or do not extend to the low temperatures found in those systems. Because methane is such an important constituent in outer planet atmospheres, we have initiated a program to measure the temperature dependence of (V-T) rates for its relaxation by appropriate collision partners. These rates are in turn used for the engineering development of, planning of, and the interpretation of data from a variety of planetary missions: Cassini/Huygens, Galileo Orbiter/Probe and Pluto-Kuiper Express.

Direct measurements of the relaxation of methane by nitrogen have been completed from 300 to 200 K in 20 K increments. This data represents the first experimental results of the methane – nitrogen system at other then room temperature. Results show the relaxation rate to be approximately 20% less then the expected values. A talk entitled "Methane ($\nu_4$) Relaxation by Nitrogen" was presented at the 34$^{rd}$ Annual Meeting of the American Astronomical Society (AAS) Division of Planetary Sciences meeting in Birmingham, AL.Current work continues on determining the rates for the relaxation of methane by nitrogen as a function of temperature down to 90 K.

Results from earlier work on the efficiency of vapor-to-crystalline solid growth in low gravity conditions was reported in a paper entitled "Zinc Crystal Growth in Microgravity" in the *The Astrophysical Journal.*

A recent collaboration has begun with researchers from the Naval Research Laboratory (NRL) to develop an eye safe LIDAR operating at 1.56 microns. The system will employ traditional high power short pulse lasers and use Raman conversion in deuterium cells to convert the 1.06 micron radiation to eye safe 1.56 microns. At present a working system has been developed and operates at up to a 45% conversion efficiency.

**Progress Report**
**Frank Ferguson**
**1 May 2002 – 30 April 2003**

The central focus of this research has been the vapor phase nucleation and growth of metals/refractory species into small particles and the aggregation of these primary particles into larger structures. These topics are part of the broader goal of understanding the conditions under which interstellar dust grains condense from stellar outflows and how these small dust grains coagulate into larger bodies such as planetesimals or planets.

There have been relatively few studies on the vapor phase nucleation of metallic or refractory species and even less agreement between data and theory. Due to this lack of data it is impossible to make reliable predictions of grain nucleation in stellar outflows. We are currently trying to develop a database of nucleation data on these refractory species to help fill this void in information. Nucleation data have been collected in our laboratory using a gas evaporation apparatus. In this system the conditions at the nucleation front are estimated using a combination of temperature measurements and a numerical model of the fluid flow and metal vapor transport. Previously, this modeling did not include depression of the concentration profile due to vapor condensation and particle growth. In the past few months we have been incorporating this contribution to the modeling using the "modal aerosol dynamics" technique. Under this technique, the complete spectrum of particle sizes is assumed to be composed of a collection of modes and each of these modes is often modeled with a simple size distribution function (e.g. a lognormal distribution). Differential equations for the moments of these size distribution functions are used to track the nucleation, growth and transport of particles.

The ultimate goal of this model is to use it in conjunction with experimental measurements to determine the conditions under which refractory materials nucleate. It is anticipated that this will require a 2D model of the chamber operation. To quicken development, the addition of the aerosol modeling has been made in stages. First, a simplified, 1D model has been developed. Although the geometry is not as realistic as a 2D model, most of the basic ingredients for the program have been developed using this model at a much quicker speed. Much of the work for the 2D model has been completed and we anticipate completing the modeling work soon.

The second research topic is how do micron-sized grains aggregate to larger bodies such as planetesimals and planets? In current theories of the early solar nebula, drag forces dominate over gravitational forces in the particle size range of 1 micron to 1 kilometer. Both theoretical and experimental works seem to indicate that particles in this intermediate range (i.e. approximately centimeters in size) will grow into porous, "fractal-like" structures. It is impossible to study the properties of such structures under terrestrial conditions since these particles tend to settle quickly once they grow to an appreciable size. Researchers at NASA-Goddard Space Flight Center are part of a European project to study such interactions under the long duration microgravity environment available on the International Space Station where such settling is eliminated. Specifically, we are responsible for a producing a unit that will generate primary particles from the vapor. These clouds of particles will be used as starting material for a coagulation experiment. Recently, we gave a presentation of our current progress in producing clouds of such particles and characterizing the initial size distribution of these particles. This presentation was given at the joint IMPF/ICAPS (International Microgravity Plasma Facility/Interactions in Cosmic and Atmospheric Particle Systems) workshop at the European Space Agency's ESTEC facility in Noordwijk, Netherlands.